AD-A060 400   HULL UNIV (ENGLAND) DEPT OF CHEMISTRY   F/G 7/3
               KINETICS OF HYDROGEN-OXYGEN AND HYDROCARBON-OXYGEN REACTIONS.(U)
               JUN 78   R R BALDWIN, R W WALKER   AFOSR-77-3215
UNCLASSIFIED   AFOSR-TR-78-1373   NL

| OF |
AD
A060 400

END
DATE
FILMED
1-79

DDC

AFOSR-TR- 78-1373

AD A060400

LEVEL

A046595

2

SC

University of Hull
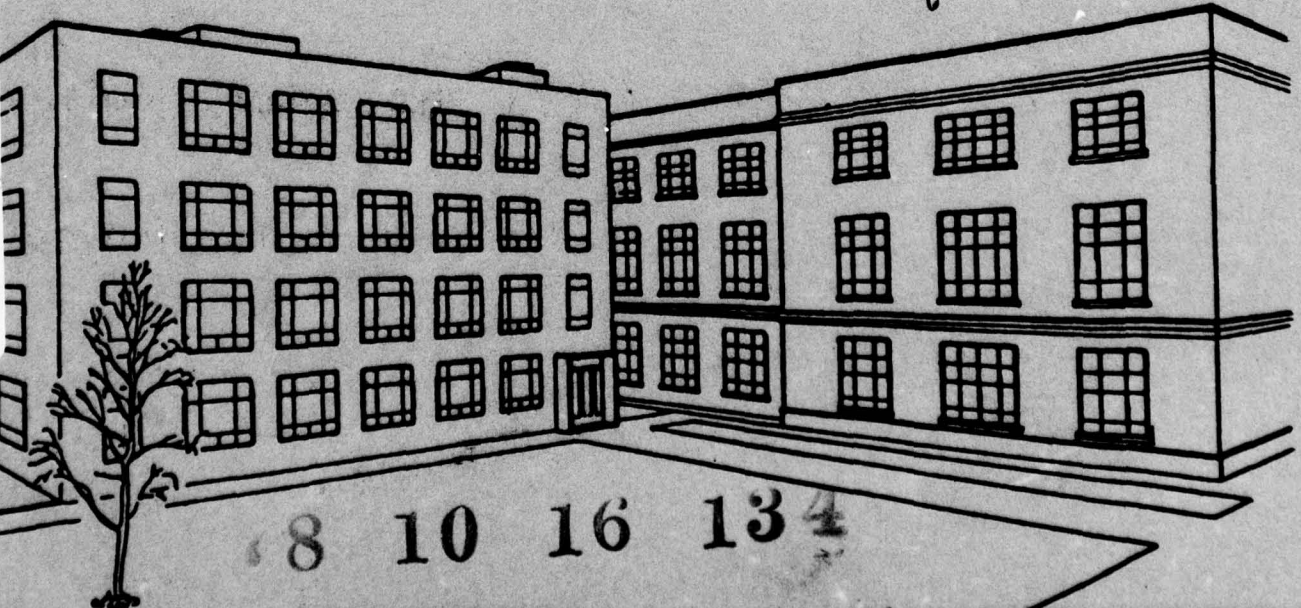
Chemistry Department

INTERIM SCIENTIFIC REPORT

GRANT NO. AFOSR-77-3215

BY RR BALDWIN & RW WALKER

D D C

RECEIVED
OCT 26 1978

D

8 10 16 134

REPORT DOCUMENTATION PAGE

**READ INSTRUCTIONS
BEFORE COMPLETING FORM**

1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
AFOSR-TR- 78-1373		

4. TITLE (and Subtitle)	5. TYPE OF REPORT & PERIOD COVERED
KINETICS OF HYDROGEN-OXYGEN AND HYDROCARBON-OXYGEN REACTIONS.	INTERIM rept. 1 Apr 77 - 30 Jun 78
	6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)	8. CONTRACT OR GRANT NUMBER(s)
ROBERT R. BALDWIN RAYMOND W. WALKER	AFOSR-77-3215

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
THE UNIVERSITY/HULL DEPARTMENT OF CHEMISTRY HULL ENGLAND HU6 7RX	2308 B2 61102F

11. CONTROLLING OFFICE NAME AND ADDRESS	12. REPORT DATE
AIR FORCE OFFICE OF SCIENTIFIC RESEARCH/NA BLDG 410 BOLLING AIR FORCE BASE, D C 20332	Jun 1978
	13. NUMBER OF PAGES
	15

14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)	15. SECURITY CLASS. (of this report)
	UNCLASSIFIED
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

COMBUSTION REACTIONS	H WITH HYDROCARBON	ACETONE FORMATION
EFFECT OF SURFACE	ALKYL RADICAL WITH OXYGEN	CARBON DIOXIDE FORMATION
RATE CONSTANTS	OXIDATION OF PROPIONALDEHYDE	HYDROPEROXY RADICAL WITH H
OH WITH CO	ACETALDEHYDE FORMATION	ATOMS
OH WITH HYDROCARBON	OXIDATION OF ISOBUTYRALDEHYDE	HYDROPEROXY RADICAL WITH HYDROCARBON (CONT)

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Refinement of the rate constants obtained from studies of the H_2+O_2 reaction at 500°C has continued. Rate constants for the reactions of H atoms and OH radicals with C_2-C_5 alkanes have been refined, and Arrhenius parameters obtained. New studies have been made of the addition of 2,2,3,3-tetramethylbutane and 2,2,3-trimethylbutane to slowly reacting mixtures of H_2+O_2 at 480°C. The mechanism of CO_2 formation in propionaldehyde oxidation, and of acetone formation in isobutyraldehyde oxidation at 440°C has been examined. Rate constants have been obtained for the initiation process and for attack of HO_2 at the various C-H bonds. The →

DD FORM 1473 1 JAN 73

homogeneous decomposition of 2,2,3,3-tetramethylbutane (TMB) in the presence of O_2 has been shown to be an excellent source of HO_2 radicals, and preliminary rate constants have been obtained for HO_2+TMB, and $HO_2+C_2H_6$ at 440°C. Interpretation of the N_2O+H_2 reaction continues.

19. (CONT)
HYDROPEROXY RADICAL WITH ALDEHYDES
THERMOCHEMISTRY OF T-BUTYL RADICALS
TETRAMETHYLBUTANE
HYDROGEN-MITRONS OXIDE REACTION

LEVEL II

GRANT AFOSR-77-3215   30th JUNE 1978

INTERIM SCIENTIFIC REPORT

Kinetics of Hydrogen-Oxygen and Hydrocarbon-Oxygen Reactions

1st April 1977 - 30th June 1978

by Baldwin, R. R., and Walker, R. W.

Chemistry Department,
The University,
HULL.

DDC
RECEIVED
OCT 26 1978
D

78 10 16 134

I N D E X

* * * * * * *

* * * * * * *

Summary

During the past year, work has been in progress in five main areas, listed below.

1. Refinement of the rate constants for the elementary steps involved in the reaction between H_2 and O_2 has continued, and a paper has now been accepted for publication.

2. Studies of the addition of alkanes and related compounds to slowly reacting mixtures of $H_2 + O_2$ have continued. Previously published rate constants for the reactions of H atoms and OH radicals with C_2-C_5 alkanes have been refined, and Arrhenius parameters suggested. New values have been obtained for 2,2,3,3-tetramethylbutane, and the reactions of the tetramethylbutyl radicals are being elucidated.

3. A computer interpretation of the yields of CO_2 and CH_3CHO in the oxidation of C_2H_5CHO, and of $(CH_3)_2CO$ in the oxidation of $i-C_3H_7CHO$ has been made. Improved rate constants for HO_2 attack at the aldehydic bond, and at the adjacent C-H bond have been obtained.

4. A computer treatment of the reaction between 2,2,3,3-tetramethyl-butane (TMB) and O_2 has indicated that it offers a useful source of HO_2 radicals, and that it should be possible to obtain rate constants for reactions of HO_2 with additives such as CO and alkanes. Preliminary values of rate constants for HO_2 + TMB, and $HO_2 + C_2H_6$ have been obtained. Arrhenius parameters for the direct molecular decomposition of TMB into i-butene and i-butane have been obtained.

5. The computer program developed earlier to interpret the results obtained in a study of the reaction between N_2O and H_2 at $600^{\circ}C$ has been applied to studies made at $500^{\circ}C$. A satisfactory prediction of the experimental results can be obtained by the use of certain combinations of rate constants, and the validity of these kinetic parameters is being examined.

*   *   *   *   *   *

1.   The hydrogen + oxygen reaction

Rate constants and rate constant ratios at $500^\circ C$ for the elementary steps in the $H_2 + O_2$ reaction have been revised to allow for the effect of self-heating of the system, the $O + H_2O_2$ reaction, and other minor refinements in the mechanism.   The results indicate that in most cases, the changes in the parameters due to the above effects are less than 10%.   New Arrhenius parameters are recommended for reactions (a), (b), and (c) between HO_2 and H atoms.

Reaction						$E/kJ\ mol^{-1}$	$A/dm^3\ mol^{-1}\ s^{-1}$
HO_2	+ H	=		2OH	(a)	7.6	5.4×10^{11}
HO_2	+ H	=	H_2	+ O_2	(b)	0	2.8×10^{10}
HO_2	+ H	=	H_2O + O		(c)	7.6	5.5×10^{10}

This work has now been accepted for publication.

The studies of the $CO + H_2 + O_2$ system, described in the last final report,[1] which enable rate constants for the reactions of OH and HO_2 radicals to be obtained, have now been published.[2]
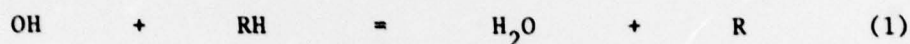
2.   Addition of hydrocarbons to slowly reacting mixtures of hydrogen and oxygen

The values of the rate constants for H and OH attack on C_2H_6, C_3H_8, n- and i-C_4H_{10} and C_5H_{12} have been re-examined to allow for the following complications:

(a)   pressure changes due to the oxidation of the hydrocarbon, which are superimposed on the pressure change due to the $H_2 + O_2$ reaction, which is used to monitor the amount of water formed;

(b)   self-heating of the reaction mixture, which affects the relationship between the observed pressure change and the amount of water formed;

(c)   removal of hydrocarbon to a small extent by attack from O atoms and HO_2 radicals.

Use of a computer treatment to analyse the effects has shown that although no single complication has a major effect, the combined consequence of them all is to approximately halve the values obtained for

the rate constants for OH attack on the hydrocarbons, but to decrease the values for H attack only slightly. By combining the results with those of other workers, the straight line plots of log k_1/k_2 against $1/T$ have been used to obtain the Arrhenius parameters (A_1/A_2) and (E_1-E_2) for attack at primary, secondary and tertiary C-H bonds in alkanes; absolute values of k_1 can be obtained from the known value of k_2, which shows a slight deviation from Arrhenius type behaviour. Use of the more limited information on k_3 at lower temperatures has permitted reasonable estimates of A_3 and E_3 to be obtained for some alkanes. This work has now been accepted for publication.

$$OH + RH = H_2O + R \qquad (1)$$
$$OH + H_2 = H_2O + H \qquad (2)$$
$$H + RH = H_2 + R \qquad (3)$$
$$H + O_2 = OH + O \qquad (4)$$

Studies are continuing on the addition of hydrocarbons and related compounds to slowly reacting mixtures of $H_2 + O_2$ in aged boric-acid-coated vessels at about $500^\circ C$ to obtain information on the rate constants and Arrhenius parameters of the elementary reactions involved in hydrocarbon oxidation. The paper on the addition of $n-C_5H_{12}$, presented at the Sixteenth International Combustion Symposium, has now been published[3] in the Symposium volume. Experimental studies with 2,2,3,3-tetramethylbutane (TMB) have now been completed, and computer analysis of the kinetic data has been carried out to obtain accurate values of k_1/k_2 and k_3/k_4, which are compared in the table with the analogous values for ethane and neopentane at $480^\circ C$.

RH	k_1/k_2	k_3/k_4
ethane	5.7 ± 0.5	44 ± 4
neopentane	10.0 ± 1.0	52 ± 5
tetramethylbutane	8.0 ± 1.0	112 ± 8

On a simple additivity basis, which has proved successful in accounting for the variation in the rate constant ratios for attack on the hydrocarbons in the homologous series of straight chain alkanes from C_2H_6 to C_5H_{12} and for variations in rate constants observed by other workers,

the rate constant ratios should vary in the proportions 1 : 2 : 3 from C_2H_6 to neo-C_5H_{12} to TMB, as all three hydrocarbons only contain primary C-H bonds. For the H atom reaction, although the value for neo-C_5H_{12} is relatively low, the change from C_2H_6 to TMB is almost that expected. For OH attack, the change from C_2H_6 to neo-C_5H_{12} is almost a factor of 2, but the value for TMB is considerably lower than expected. Differences in the A factor rather than activation energy effects are the most likely cause. Use of independent data for reactions (2) and (4) gives $k_1 = 3.1 \times 10^9$ and $k_3 = 6.4 \times 10^8$ dm^3 mol^{-1} s^{-1} for TMB at $480^{\circ}C$.

A complete analysis of the products when TMB is the additive has been carried out over a wide range of mixture composition. Isobutene is the only major initial product and is formed in near-quantitative yield, the minor initial products being C_3H_6, 2,3,3-trimethylbut-1-ene, 2,2-dimethyloxiran, HCHO, and CH_4, all formed in about 1% yield. No evidence has been found for the presence of O-ring compounds containing the same number of carbon atoms as tetramethylbutane. Preliminary analysis suggests that at least 96% of the TMB radicals decompose into i-C_4H_8 and t-C_4H_9 radicals rather than undergo oxidation, presumably because of the high degree of steric strain in the central C-C bond. A full interpretation of the results leading to rate constants for some of the elementary steps is proceeding.

A detailed examination has been made of the addition of 2,2,3-trimethylbutane to hydrogen + oxygen mixtures. The kinetic results indicate that the hydrocarbon is somewhat faster by radical attack than TMB, as expected because of the replacement of a CH_3 group by a tertiary C-H group. The major initial products are i-C_4H_8 and C_3H_6, formed in nearly equal yields, although there are significant yields of 2,3,3-trimethylbut-1-ene and CH_4, together with several minor products. At present, interpretation of the kinetic results is being carried out to determine the rate constants for H and OH attack on the hydrocarbon. When these parameters are available, it should be possible to calculate the proportions of the three species of radical formed from 2,2,3-trimethylbutane, which is necessary in order to interpret the product distribution.
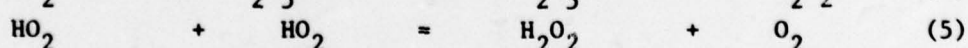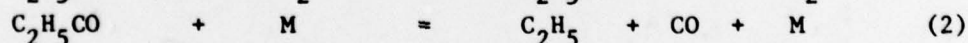
The results obtained earlier with i-C_4H_{10} as additive have now

been fully interpreted in quantitative terms, and the two papers, referred to in the last interim report,[4] have been condensed into a single paper which has been accepted for publication. A value of 6.8×10^7 has been evaluated for k_5, and when combined with a low temperature measurement gives $A_5 = 6.9 \times 10^9$ 1 mol^{-1} s^{-1} and $E_5 = 7.0$ kcal mol^{-1}. From the measurements of the yields of isobutene oxide and 3-methyloxetan, a value of $k_6/k_7 = 4.1 \pm 0.4$ is obtained. Use of the rather uncertain value of the rate constant for the decomposition of i-butyl radicals, together with the best thermochemical data available for reaction (8), gives $k_6 = 1.83 \times 10^5$ s^{-1} and $k_7 = 4.45 \times 10^4$ s^{-1}. No other experimental value is available for k_6 nor for any similar reaction involving the transfer of a tertiary H atom.

$$CH_3CH(CH_3)CH_2 \quad + \quad O_2 \quad = \quad (CH_3)_2C=CH_2 \quad + \quad HO_2 \quad (5)$$

$$CH_3CH(CH_3)CH_2O_2 \quad \rightarrow \quad CH_3C(CH_3)(CH_2OOH) \quad (6)$$

$$CH_3CH(CH_3)CH_2O_2 \quad \rightarrow \quad CH_3CH(CH_2OOH)CH_2 \quad (7)$$

$$CH_3CH(CH_3)CH_2 \quad + \quad O_2 \quad = \quad CH_3CH(CH_3)CH_2O_2 \quad (8)$$

3. The oxidation of aldehydes

In an earlier study of the oxidation of C_2H_5CHO at $440°C$ in aged boric-acid-coated vessels, a study of the kinetic behaviour of the reaction for one mixture enabled the rate constants k_1 and k_4 to be evaluated. Although the main reaction products are C_2H_4, CO and H_2O_2, resulting from the reaction sequence (1)-(5), significant yields (ca 15%) of CO_2 and of CH_3CHO are also formed, and their mechanism of formation has now been examined.
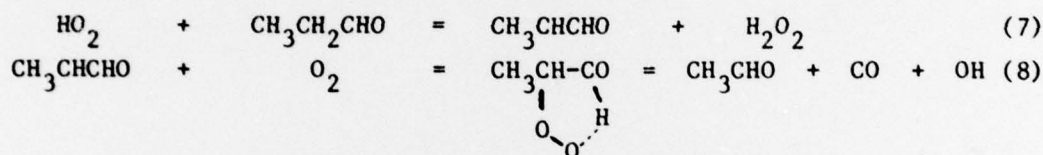
$$C_2H_5CHO \quad + \quad O_2 \quad = \quad C_2H_5CO \quad + \quad HO_2 \quad (1)$$

$$C_2H_5CO \quad + \quad M \quad = \quad C_2H_5 + CO + M \quad (2)$$

$$C_2H_5 \quad + \quad O_2 \quad = \quad C_2H_4 \quad + \quad HO_2 \quad (3)$$

$$HO_2 \quad + \quad C_2H_5CHO \quad = \quad C_2H_5CO \quad + \quad H_2O_2 \quad (4)$$

$$HO_2 \quad + \quad HO_2 \quad = \quad H_2O_2 \quad + \quad O_2 \quad (5)$$

The $[CO_2]/[CO]$ ratio in the products increased with increase in the concentration of O_2, and decreased with increasing addition of inert gas, suggesting a competition between reactions (6) and (2).

$$C_2H_5CO \quad + \quad O_2 \quad = \quad C_2H_5CO_3 \quad \rightarrow \quad C_2H_4 + CO_2 + OH \quad (6)$$
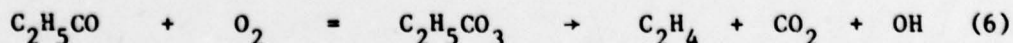
A more detailed study of the CO_2 yields was made, since it was hoped that

the competition between reactions (2) and (6) would enable the efficiency of different inert molecules in reaction (6) to be examined. This study showed that the $[CO_2]/[CO]$ ratio decreased sharply in the early stages of reaction to an almost steady value, and then rose again in the later stages. This decrease can only be explained by the occurrence of a surface formation of CO_2 in parallel with the homogeneous reaction (6). Since the reaction accelerates in the early stages, due to the dissociation of H_2O_2, this surface formation decreases in importance relative to the homogeneous processes as the reaction proceeds, thus accounting for the decrease in the $[CO_2]/[CO]$ ratio. In confirmation, significantly higher yields of CO_2 are found in a smaller diameter vessel. A computer program has been written to interpret the full mechanism, including the formation of CH_3CHO, which is considered to result from the reaction sequence (7) and (8):
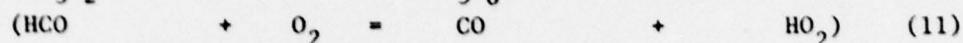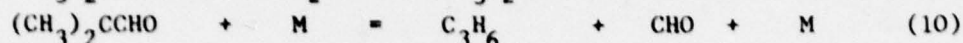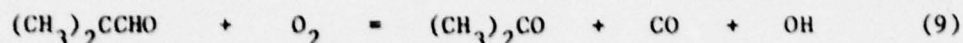
$$HO_2 \quad + \quad CH_3CH_2CHO \quad = \quad CH_3CHCHO \quad + \quad H_2O_2 \qquad (7)$$

$$CH_3CHCHO \quad + \quad O_2 \quad = \quad CH_3CH\text{-}CO \quad = \quad CH_3CHO + CO + OH \quad (8)$$

A detailed interpretation of the results for a wide range of mixtures gives the optimal value of the parameters as $k_1 = 0.077$ 1 mol^{-1} s^{-1}, $k_4/k_5^{\frac{1}{2}} = 36$ $(1$ mol^{-1} $s^{-1})^{\frac{1}{2}}$, $k_7/k_5^{\frac{1}{2}} = 2.5$ $(1$ mol^{-1} $s^{-1})^{\frac{1}{2}}$, and $k_6/k_2 = 0.108$ (for $M = N_2$).

Since $k_5 = 2 \times 10^9$ 1 mol^{-1} s^{-1}, $k_4 = 1.59 \times 10^6$ 1 mol^{-1} s^{-1}, $k_7 = 1.1 \times 10^5$ 1 mol^{-1} s^{-1}. The value of k_7 is higher, by a factor of about 4, than preliminary estimates of the rate constant for HO_2 with a secondary CH_2 group in an alkane. This work has now been accepted for publication.

A similar study has been made of the oxidation of $i\text{-}C_3H_7CHO$. The main products are C_3H_6, CO and H_2O_2, but significant amounts of acetone (up to 15%) are obtained, and smaller amounts of CO_2 (up to 6%) and propene oxide (up to 3%). The variation of $[CO_2]/[CO]$ with time suggests that at least part of the CO_2 is formed by a surface process, but the detailed analysis made with C_2H_5CHO is not possible because of the limited accuracy consequent on the smaller yield. The yield of $(CH_3)_2CO$ varies markedly with the concentration of O_2, and this suggests

a competition between the reaction (9), analogous to reaction (8) for C_2H_5CHO, and (10).

$$(CH_3)_2CCHO \quad + \quad O_2 \quad = \quad (CH_3)_2CO \quad + \quad CO \quad + \quad OH \qquad (9)$$

$$(CH_3)_2CCHO \quad + \quad M \quad = \quad C_3H_6 \quad + \quad CHO \quad + \quad M \qquad (10)$$

$$(HCO \quad + \quad O_2 \quad = \quad CO \quad + \quad HO_2) \qquad (11)$$

The yield of acetone also increases with time, and this is attributed to the increasing formation of the $(CH_3)_2CCHO$ radical by attack of the relatively unselective OH radical on the parent aldehyde; this attack increases in importance as the reaction proceeds due to build up and subsequent dissociation of H_2O_2. The rate constant for HO_2 and OH attack at the t-C-H bond can thus be obtained, and a computer program is being used to obtain the optimal values. This treatment is possible because $(CH_3)_2CO$ is a stable product, but it cannot be used in the case of the oxidation of C_2H_5CHO where the intermediate, CH_3CHO, is much more reactive.
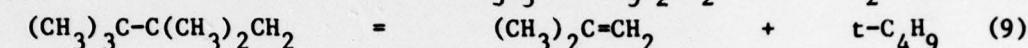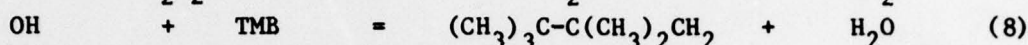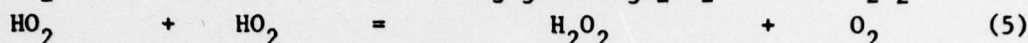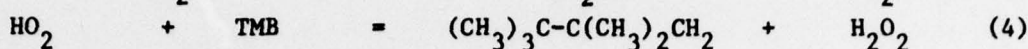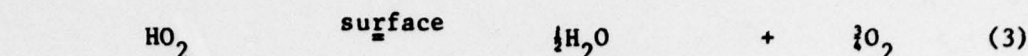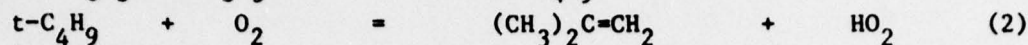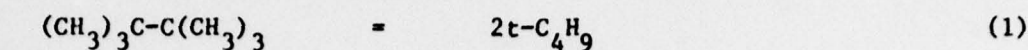
4. The oxidation of 2,2,3,3-tetramethylbutane

In KCl-coated vessels, which are highly efficient for the destruction of HO_2 radicals, and reasonably efficient for the destruction of H_2O_2, the rate of decomposition of 2,2,3,3-tetramethylbutane (TMB) has been found experimentally to be represented with reasonable accuracy by equation (i).

$$-d[TMB]/dt \quad = \quad k_{obs}[TMB]^1[O_2]^0 \qquad (i)$$

This is consistent with a basic mechanism involving reactions (1)-(3), and (7), which give the rate expression (ii).

$$-d[TMB]/dt \quad = \quad k_1[TMB]^1[O_2]^0 \qquad (ii)$$

However, careful measurements show that k_{obs} increases slightly as the concentration of TMB is increased. k_{obs} also increases on addition of inert gas, and this is attributed to an increasing contribution from reaction (4), consequent on the reduction in the diffusion controlled destruction of HO_2, and to a contribution from reaction (8) consequent on the increased dissociation of H_2O_2 by reaction (6) relative to its surface destruction by reaction (3). The full mechanism thus involves reactions (1)-(9) listed below.

$$(CH_3)_3C-C(CH_3)_3 \quad = \quad 2t-C_4H_9 \quad\quad\quad (1)$$

$$t-C_4H_9 \quad + \quad O_2 \quad = \quad (CH_3)_2C=CH_2 \quad + \quad HO_2 \quad (2)$$

$$HO_2 \quad \overset{surface}{=} \quad \tfrac{1}{2}H_2O \quad + \quad \tfrac{3}{4}O_2 \quad (3)$$

$$HO_2 \quad + \quad TMB \quad = \quad (CH_3)_3C-C(CH_3)_2CH_2 \quad + \quad H_2O_2 \quad (4)$$

$$HO_2 \quad + \quad HO_2 \quad = \quad H_2O_2 \quad + \quad O_2 \quad (5)$$

$$H_2O_2 \quad + \quad M \quad = \quad 2OH \quad + \quad M \quad (6)$$

$$H_2O_2 \quad \overset{surface}{=} \quad H_2O \quad + \quad \tfrac{1}{2}O_2 \quad (7)$$

$$OH \quad + \quad TMB \quad = \quad (CH_3)_3C-C(CH_3)_2CH_2 \quad + \quad H_2O \quad (8)$$

$$(CH_3)_3C-C(CH_3)_2CH_2 \quad = \quad (CH_3)_2C=CH_2 \quad + \quad t-C_4H_9 \quad (9)$$

By correction of k_{obs} for the small chain due to HO_2 and OH attack on TMB, values of k_1 have been obtained over the temperature range 420-540°C, and the log k_1 against $1/T$ plot gives $E_1 = 70.6$ kcal mol^{-1}, compared to 71.0 kcal mol^{-1} from the log k_{obs}, $1/T$ plot for [TMB] ⩽ 1 Torr. Combination with values obtained by Tsang[5] using a shock-tube technique over the range 985-1141 K gives the Arrhenius parameters $A_1 = 6.0 \times 10^{16}$ s^{-1}, $E_1 = 69.4 \pm 0.5$ kcal mol^{-1}. These values, and their implications for the thermochemistry of the $t-C_4H_9$ radical have been discussed in an earlier report[1] and in a published paper.[6]

Before starting detailed studies on the use of the oxidation as a source of $t-C_4H_9$ and HO_2 radicals, a computer program has been used to predict the behaviour of the system, so as to establish the experimental conditions that are most likely to repay investigation. The computer program requires the parameters k_1, $k_3/k_5^{\frac{1}{2}}$, $k_4/k_5^{\frac{1}{2}}$, k_6 and k_7, and reasonable estimates of these can be made. From the computer analysis, the following conclusions can be drawn.

(a) For the "standard" mixture (TMB = 2 Torr, O_2 = 30 Torr, N_2 = 28 Torr), the chain contribution to removal of TMB is less than 15% over the temperature range 440-540°C in a KCl-coated vessel, which has a highly efficient surface for the destruction of HO_2 radicals, and also has a moderately efficient surface for the destruction of H_2O_2.

(b) The percentage contribution of the chain reaction only changes slightly over the temperature range 440-540°C. This arises because the decreasing chain contribution from HO_2 attack (resulting from the increasing

importance of reaction (5) relative to reactions (3) and (4)) as the temperature rises is compensated by an increasing contribution from the OH chain (resulting from the increased concentration of OH radicals arising from reaction (6)) as the temperature rises.   As a consequence, the plot of log k_{obs}, the experimental rate constant against 1/T gives an activation energy very close to the true value for reaction (1).

(c)   The computer treatment shows that at 440°C, the chain is almost entirely due to the HO_2 radical, and that the chain length increases with increase in the concentration of TMB, and with addition of inert gas. This increase in the observed rate constant can be used to obtain the rate constant for the reaction of HO_2 radicals with TMB, and interpretation of the experimental results over a range of TMB concentration and N_2 addition using the computer program, gives a preliminary value $k_4/k_5^{\frac{1}{2}} = 0.38 \pm 0.04$ $(dm^3\ mol^{-1}\ s^{-1})^{\frac{1}{2}}$.   Since $k_5 = 2 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$, $k_4 = (1.70 \pm 0.20) \times 10^4$ at 440°C.

(d)   OH   +   CO   =   H   + CO_2 (10)

   HO_2 +   CO   =   OH   + CO_2 (11)

The computer program has been extended by incorporating reactions (10) and (11) so as to examine the feasibility of studying reaction (11) by addition of CO to reacting TMB + O_2 mixtures.   Results from the computer program indicate clearly that at 440°C, measurement of the ratio $d[CO_2]/d[TMB]$ should enable the rate constant ratio $k_{11}/k_5^{\frac{1}{2}}$ to be evaluated.   The program also indicates that even at 540°C, the contribution of reaction (10) to CO_2 formation can be estimated with sufficient accuracy to enable $k_{11}/k_5^{\frac{1}{2}}$ to be evaluated at this temperature also. It is hoped to start this experimental study in the near future.

(e)   The computer program has also been extended to allow examination of the potential of the TMB + O_2 system as a source of HO_2 radicals to study their reactions with added hydrocarbons and related compounds. If HO_2 radicals are solely destroyed by reaction (3), stationary state treatment of the basic mechanism involving reactions (1)-(3) and (12) gives expression (iii).

   HO_2 +   RH   = H_2O_2 +   R   (12)
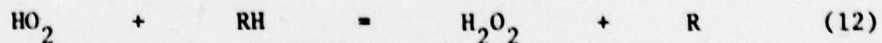
   $d[RH]/d[TMB]$ = $2k_{12}[RH]/k_3$ (iii)

If, however, HO_2 radicals are removed by reaction (5) only, and if the simplifying assumption is made that all H_2O_2 formed is destroyed by reaction (7), the relative rates of consumption are then given by expression (iv).
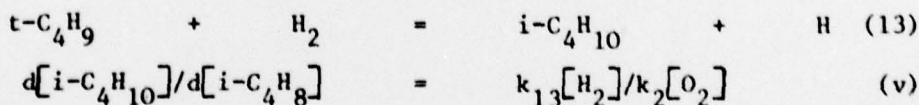
$$d[RH]/d[TMB] \quad = \quad k_{12}[RH]/(k_1k_5[TMB])^{\frac{1}{2}} \qquad (iv)$$

Depending on the nature of the termination process, $d[RH]/d[TMB]$ should thus be independent of $[TMB]$ or proportional to $[TMB]^{-\frac{1}{2}}$.

Computer analysis, using reasonable estimates of rate constants and rate constant ratios, shows that these extreme relationships, although approached under certain conditions, are not achieved because of dissociation of H_2O_2 and because of complications caused by attack of HO_2 and OH both on TMB and on RH.   The analysis also shows that little information is gained by varying the concentration of RH, and that varying the concentration of TMB, and of added inert gas, is more useful. The results also show that the presence of OH radicals will not prevent an accurate determination of k_{12} in the temperature range 420-440°C;   the interference at high temperatures is now being examined.

Experimental study of the addition of C_2H_6 to the TMB + O_2 system has thus been started at a temperature of 440°C.   Preliminary experiments have shown that several different mixture compositions give consistent values for the ratio $k_{12}/k_5^{\frac{1}{2}} = 0.28$ $(dm^3 \ mol^{-1} \ s^{-1})^{\frac{1}{2}}$, from which a preliminary value of $k_{12} = 1.25 \times 10^4 \ dm^3 \ mol^{-1} \ s^{-1}$.   Further measurements over a range of temperatures is planned.

The reaction between TMB and O_2 is also being used as a source of $t-C_4H_9$ radicals to enable their reactions to be studied.   Addition of H_2 results in formation of $i-C_4H_{10}$ by reaction (13), which competes with reaction (2), so that the relative rates of formation of $i-C_4H_{10}$ and $i-C_4H_8$ are given by equation (v).

$$t-C_4H_9 \qquad + \qquad H_2 \qquad = \qquad i-C_4H_{10} \qquad + \qquad H \quad (13)$$

$$d[i-C_4H_{10}]/d[i-C_4H_8] \qquad = \qquad k_{13}[H_2]/k_2[O_2] \qquad (v)$$

Corrections to the results are necessary to allow for the $i-C_4H_8$ formed in the chain consumption of TMB, due to the decomposition of the TMB radical, and for the formation of $i-C_4H_{10}$ and $i-C_4H_8$ formed in the direct molecular process (14).

This molecular reaction has been studied separately over the temperature range 420-540°C, and the Arrhenius parameters $A_{14} = 7.8 \times 10^{13}$ s^{-1}, $E_{14} = 65.7 \pm 0.5$ kcal mol^{-1} have been obtained. A paper on the direct molecular decomposition has now been published.[7] Arrhenius parameters for reactions (2) and (13) remain to be accurately determined, but it is quite clear that the activation energy of (2) is low, as suggested previously, and does not exceed about 5 kcal mol^{-1}.

$$(CH_3)_3CC(CH_3)_3 \quad = \quad i\text{-}C_4H_8 \quad + \quad i\text{-}C_4H_{10} \qquad (14)$$
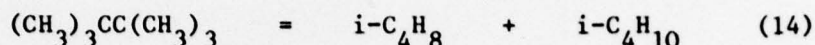
5. The reaction between hydrogen and nitrous oxide

As reported previously, the reaction between H_2 and N_2O has been studied mass spectrometrically at 500°C to complement an extensive earlier investigation[8] at 600°C. The mechanism developed for the studies at the higher temperature has been applied to the results at 500°C and appears to give a very satisfactory interpretation of the data. The sensitivity of the optimised kinetic parameters to changes in the 'known' rate constants is currently being examined. When the optimum rate constants become available, it should be possible to determine Arrhenius parameters for several of the elementary steps involved. It is intended to submit this work for publication shortly.

Studies of the addition of C_2H_6 to slowly reacting mixtures of $H_2 + N_2O$ at 550°C, referred to in the last interim report,[4] although promising, has been suspended as the research worker carrying out the investigation has now left the group.

References

1. R. R. Baldwin and R. W. Walker.
    Final Report on Grant AFOSR-73-2450, March 1977.

2. G. M. Atri, R. R. Baldwin, D. Jackson, and R. W. Walker.
    Combustion and Flame, 1977, 30, 1.

3. R. R. Baldwin, Mrs. J. P. Bennett, and R. W. Walker.
    Sixteenth Symp. (Int.) on Combustion, The Combustion Institute,
    1976, p.1041.

4. R. R. Baldwin and R. W. Walker.
    Progress Report No. 1 on Grant AFOSR-77-3215, September 1977.

5. W. Tsang.
    J. Chem. Phys., 1966, 44, 4283.

6. G. M. Atri, R. R. Baldwin, G. A. Evans, and R. W. Walker.
    J. Chem. Soc., Faraday I, 1978, 74, 366.

7. R. R. Baldwin, G. A. Evans, and R. W. Walker.
    J. Chem. Soc., Faraday I, 1978, 74, 1329.

8. R. R. Baldwin, A. Gethin, J. Plaistowe, and R. W. Walker.
    J. Chem. Soc., Faraday I, 1975, 71, 1265.

* * * * * * * *

Publications

1. R. R. Baldwin, Mrs. J. P. Bennett, and R. W. Walker.
    Sixteenth Symp. (Int.) on Combustion, The Combustion Institute,
    1976, p.1041.
    "Rate constants for elementary steps in hydrocarbon oxidation".

2. G. M. Atri, R. R. Baldwin, D. Jackson, and R. W. Walker.
    Combustion and Flame, 1977, 30, 1.
    "The reaction of OH radicals and HO_2 radicals with carbon monoxide".

3. R. R. Baldwin, J. C. Plaistowe, and R. W. Walker.
    Combustion and Flame, 1977, 30, 13.
    "The mechanism of conjugate alkene formation and the importance of
     surface reactions in hydrocarbon oxidation".

4. G. M. Atri, R. R. Baldwin, G. A. Evans, and R. W. Walker.
    J. Chem. Soc., Faraday I, 1978, 74, 366.
    "Decomposition of 2,2,3,3-tetramethylbutane in the presence of oxygen".

Publications / continued

5. R. R. Baldwin, G. A. Evans, and R. W. Walker.
    J. Chem. Soc., Faraday I, 1978, 74, 1329.
    "Molecular decomposition of 2,2,3,3-tetramethylbutane".

6. R. R. Baldwin, K. A. Lewis, and R. W. Walker.
    Paper accepted for publication by the Journal of the Chemical
    Society, Faraday I.
    "Carbon dioxide formation in the oxidation of propionaldehyde".

7. R. R. Baldwin and R. W. Walker.
    Paper accepted for publication by the Journal of the Chemical
    Society, Faraday I.
    "Rate constants for the hydrogen + oxygen system, and for H atoms
     and OH radicals + alkanes".

*   *   *   *   *   *   *   *

Conferences attended and Lectures presented

Professor Baldwin gave an invited lecture entitled "Problems
and Progress in Hydrocarbon Oxidation", at the Autumn Meeting of the
Chemical Society, held at the University of Aberdeen in September 1977.

Dr. Walker attended the "Fifth International Symposium on Gas
Kinetics", held in Manchester in July 1977 and presented a paper
entitled "The Decomposition of Hexamethylethane in the Presence of
Oxygen".

*   *   *   *   *   *   *   *

Personnel

Mr. I. A. Pickering (B.Sc., Hull 1978) has accepted a technician
post in the group from July, 1978.

Mr. A. P. Keen (B.Sc., Hull 1977) joined the group in September
1977, financed by Grant AFOSR-77-3215.

Mr. D. G. Malcolm (B.Sc., Hull 1978) and Mr. M.W.M. Hisham
(B.Sc., University of Sri Lanka) will join the group in September 1978.

*   *   *   *   *   *   *   *